BIODEGRADATION OF CELLULOSE ESTERS: COMPOSTING OF CELLULOSE ESTER-DILUENT MIXTURES

CHARLES M. BUCHANAN,* DEBRA D. DORSCHEL, ROBERT M. GARDNER, RON J. KOMAREK, and ALAN W. WHITE

Research Laboratories
Eastman Chemical Company
P.O. Box 1972, Kingsport, Tennessee 37662

ABSTRACT

A number of polymers such as polylactic acid (PLA), polycaprolactone (PCL), polyhydroxybutyrate (PHB), Matter-Bi, cellulose acetate (CA) with different degrees of substitution (DS), and cellulose ester–diluent mixtures have been evaluated in a static, bench-scale simulated municipal compost environment. Of the polymers evaluated, cellulose acetate (DS < 2.2), poly(hydroxybutyrate-co-valerate) (PHBV), and PCL exhibited the fastest composting rates, completely disappearing after 14 days. Optically clear resins were prepared from CA (DS = 2.06) and triethylcitrate (TEC) by thermal compounding, and the resins were converted to compression-molded film and injection-molded bars for composting studies. A series of miscible blends consisting of cellulose acetate propionate (CAP) and poly(ethylene glutarate) (PEG) or poly(tetramethylene glutarate) (PTG) were also prepared and evaluated in composting. In addition to measured weight loss, samples were removed from the compost at different intervals and evaluated by gel permeation chromatography and ¹H NMR. As expected, the CA/TEC films disappeared rapidly upon composting while the injection-molded bars exhibited weight losses of 10–12%. For the CAP/polyester blends, the type of polyester (PEG versus PTG) in the blend made no difference in composting rates. In general, as the DS of the CAP decreased and the amount of polyester in the blend increased, the rate of composting and

the weight loss due to composting increased. When the CAP was highly substituted, almost all of the weight loss was ascribed to loss to polyester. When the DS of the CAP was below approximately 2.0, both components degraded.

INTRODUCTION

The concept of biodegradable polymers as a solution to the disposal of solid waste is certainly not new. In a series of patents and reports in the early 1970s, Potts et al. demonstrated that polycaprolactone (PCL) was a suitable biodegradable polymer for many applications [1]. Potts et al. also showed that PCL was miscible or partially miscible with a wide range of the other polymers, which opened the door to the use of polymer blends or composites as biodegradable materials. In part, the interest in biodegradable polymers during this period of time was driven by the oil embargo and the expected shortage of petroleum as a feedstock for synthetic polymers. Over time, the fear of oil shortages waned. Furthermore, due to material cost and deficiencies, biodegradable polymers never fulfilled the expectations and hopes of that period. Consequentially, interest in biodegradable polymers faded. In the late 1980s it began to become apparent to many that available landfill space was becoming scarce in many metropolitan areas of the United States and Europe, leading to a renewed interest in biodegradable polymers and the use of composting, along with recycling and landfill, as a component for the solution of the emerging solid waste disposal crisis. Much of the research in the period from 1989 to the present has focused on starch or starch composites as new biodegradable alternatives to traditional synthetic polymers [2]. Other polymers, including polyalkanoates [e.g., polyhydroxybutyrate (PHB)] as a typical example, have also received considerable attention [3]. Very recently, it has been proposed that cellulose esters, e.g., cellulose acetate (CA), be considered as potentially useful polymers in biodegradable applications [4–11].

Historically, there has been considerable confusion regarding the biodegradation potential of cellulose esters. It was generally accepted that cellulose esters with a degree of substitution less than 1.0 will degrade from attack of microorganisms at the unsubstituted residues of the polymers, and that the ether linkages to the cellulose backbone are generally resistant to microbial attack [12]. Work by Stutzenberger and Kahler indicated that CA was a poor substrate for microbial attack [13]. Conflicting evidence was provided by Reese who isolated cellulolytic filtrates which deacetylated soluble CA (DS = 0.76) and insoluble cellobiose octaacetate [14]. Additional early evidence as to the biodegradation potential of CA was provided by Cantor and Mechalas [15]. Cantor and Mechalas demonstrated that reverse-osmosis membranes prepared from CA with a DS = 2.5 suffered loses in semipermeability due to microbial attack. Since 1992 there have been several reports which clearly demonstrate that CA having a DS of less than approximately 2.5 is inherently biodegradable under both aerobic [4, 6] and anaerobic [7] conditions, and that many cellulose acetates are readily compostable [5, 8–11]. A general finding was that as the DS of the CA decreased, the rate of biodegradation increased; below a DS of ca. 2.1, composting rates of CA approached or exceeded that of many other commercial biodegradable polymers. Very recently, Komarek et al. showed, via

aerobic biodegradation of radiolabeled cellulose propionates, that cellulose propionates below a DS of ca. 1.85 are also potentially useful as biodegradable polymers [6]. This work indicates that as the DS and the length of the acyl side group decreases, the rate of biodegradation increases; longer adaptation periods, relative to CA, were also required for the cellulose propionates.

Although careful consideration has been given to the biodegradation of cellulose esters, scarce attention has been paid to the biodegradation of formulated resins consisting of cellulose esters and diluents. This is no small matter as the melt processing temperature of most cellulose esters exceeds that of the decomposition temperature of the cellulose esters, which implies that most cellulose esters must be plasticized if they are to be used in thermoplastic applications [16]. Examining the biodegradation of a formulation consisting of two or more components imparts a new level of complexity to the problem. With polymer–diluent mixtures, the question of morphology becomes paramount. Also, with homogeneously mixed polymer–diluent or polymer–polymer mixtures, the interesting question of how the biodegradation rate of one component influences the biodegradation rate of the other component is raised.

In this account we describe the application of bench-scale composting methodology developed in our laboratories to a number of commercially available polymers that are currently being evaluated in many laboratories. This work provides a benchmark of the relative composting rates expected for these polymers in an efficient municipal window composting operation. We also report some preliminary work involving the application of this composting methodology to cellulose acetate–triethylcitrate (polymer–diluent) mixtures and to cellulose acetate propionate–polyester (polymer–polymer) blends.

MATERIALS AND METHODS

L-Polylactic acid (PLLA) and 1/1 D,L-polylactic acid (PDLLA) was obtained from Birmingham Polymers. Poly(hydroxybutyrate) (PHB) and poly(hydroxybutyrate-*co*-valerate [90/10]) (PHBV) are commercially available from Zeneca Bio-Products. Polycaprolactone (PCL) was purchased from Union Carbide, and Matter-Bi (Matter-Bi is presumably a blend of starch or modified starch and other polymers such as polyvinyl alcohol and polyacrylics [2b]) is commercially available from Novamont. Cellulose triacetate (CTA, DS = 2.97) and cellulose acetate CA398-30 (DS = 2.52) are commercially available and were obtained from Eastman Chemical Company. The remaining cellulose acetates were obtained by aqueous hydrolysis of either CTA or the CA having a DS of 2.52 [17]. Cellulose acetate propionate, having a DS of 2.75 (DS_{Ac} = 0.01, DS_{Pr} = 2.74), is commercially available from Eastman Chemical Company (Kingsport, Tennessee). The remaining cellulose acetate propionates were obtained by acid-catalyzed, aqueous hydrolysis of this DS 2.75 CAP [17]. All of these CAPs had a very low acetyl content (DS_{Ac} = 0.01–0.05) and can be considered to be essentially cellulose propionates. Poly(ethylene glutarate) (PEG) and poly(tetramethylene glutarate) (PTG) were prepared by the condensation polymerization of dimethyl glutarate and the appropriate diol using $(Ti(O^iPr)_4$ as the catalyst.

First scan DSC heating curves were obtained for the cellulose acetates using a DuPont 912 differential scanning calorimeter spectrometer. The samples were heated from 25 to 300°C at a heating rate of $20° \cdot min^{-1}$. The reported melting temperatures are nonequilibrium melting temperatures.

Films were prepared by solvent casting and by thermal processing. With the exception of CTA, the solvent for the cellulose acetates (20% solids) was acetone containing 3–7% water. The solvent for CTA, PHBV, and PCL was $CHCl_3$. The solution was poured onto a metal plate and a draw blade with a 15-mil well was used to give a thin film. PHB, PLLA, and PDLLA films were prepared by compression molding. Matter-Bi film was prepared by a blown film process. In all cases involving blends, the mixtures were prepared by thermal compounding and characterized according to previously described methods [16, 18, 19]. The cellulose acetate-triethylcitrate (CA/TEC) compositions were similarly prepared. The film thickness ranged from 2 to 8 mil. Injection-molded parts were 122 mil thick and were obtained as previously described [20].

Two types of composting studies were generally conducted. In one case, each compost unit contained a minimum of 15 test films and 10 Matter-Bi films which served as an internal positive control. Results reported herein are average values for all films in each individual unit. With the exception of PCL and, in one case, PLA, the films were added to the composting unit along with the synthetic compost mixture. Because of the low melting temperature of PCL, the PCL films were not added until completion of the thermophilic phase. Also, due to the relative low T_g of PLA, two studies were conducted. In one study, the PLA films were added at the beginning of the composting cycle (30-day experiment) and, in the second, the PLA films were added at the end of the thermophilic phase (24-day experiment). PHB, PHBV, and PCL were evaluated over a 14-day composting period. The cellulose acetates having a DS of 1.74, 1.86, 2.06, 2.21, 2.52, and 2.97 were evaluated over either a 14-day or a 30-day composting cycle. In the second type of study, each compost unit contained 30–35 films. Three to five films were removed every 3–5 days and characterized.

The details of the compost unit design, the control system, the compost mixture, compost characterization, and methods for characterization of samples removed from the compost have been extensively described elsewhere [5].

RESULTS AND DISCUSSION

General Composting

The primary criteria that we use in screening polymers in composting are initial breakup of the film within the first few days and total weight loss. Unless a film fractures into small enough pieces that will permit their passage through a screening operation commonly employed in many municipal composting operations, the films will be removed by the screening operation and will ultimately be landfilled. This, of course, defeats the entire purpose of developing a compostable polymer. Film breakage must be followed by complete mineralization of the fragments, and total weight loss is often a good indicator of mineralization. We generally make no effort to distinguish between chemical degradation and biological degradation in our composting methodology. Undoubtedly, with certain substrates,

both chemical and biological degradation coexist. In fact, we believe that one can take advantage of the changes in compost pH and temperature in designing polymers so that these processes will aid in the fragmentation and ultimate biological degradation of the polymeric substrate. Ultimately, complete mineralization of the substrate must be demonstrated but that is best accomplished using respirometry and radiochemical labeling techniques [4, 6]. Hence, the methodology described in this account models the first step of composting and serves as a predictor of ultimate mineralization.

Figure 1 provides the % weight loss for some of the potentially biodegradable polymers we have evaluated in our laboratories. The number of days given in parentheses is the length of the composting cycle, and the value following the CA samples is the total DS for the CA. The first two entries are for PLA films which were added to the compost after completion of the thermophilic phase (composting cycle = 24 days), while the next two entries are for the PLA films which were present in the compost for the entire composting cycle (composting cycle = 30 days). The experiment was conducted in this manner due to the relative low T_g (ca. 55°C) of the PLA which is exceeded during the thermophilic phase. As can be seen, in the case where the PLA did not experience the temperatures associated with the peak thermophilic phase (60–65°C, vide infra), the weight loss was minimal. When the PLA was present for the entire composting cycle, the % weight loss increased. Interestingly, in the latter case the PDLLA films showed over twice the % weight loss observed for the PLLA films which we believe is likely due to the fact that the PDLLA was entirely amorphous while the PLLA is highly crystalline. In both cases the PLA films remained intact, i.e., they did not break up into smaller fragments. As the next entry illustrates, PCL (added after the thermophilic phase) completely disintegrated (no pieces could be recovered following an extensive screening operation). Matter-Bi was a particularly interesting case. Approximately 50% weight loss
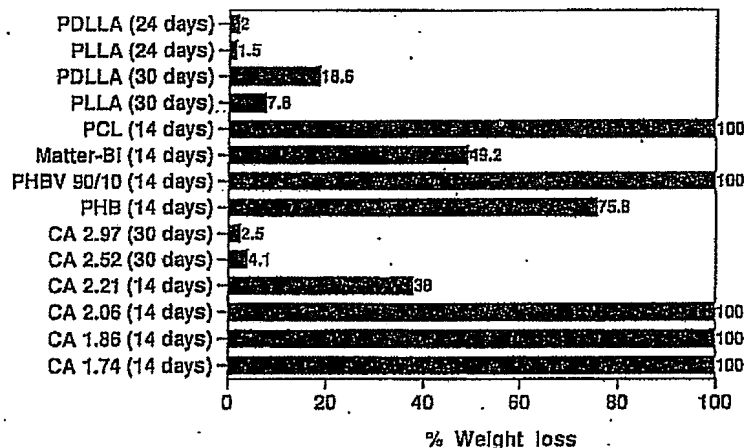

FIG. 1. The % weight loss observed for selected potentially compostable polymers in a bench-scale simulated composting environment. The numbers in parentheses reflect the length of the composting cycle while the numbers following CA indicate the degree of substitution.

was achieved very rapidly, after which an intact, flexible film remained. When the composting cycle was extended to 180 days, no changes in the remaining Matter-Bi film was observed. Iodine staining demonstrated that the starch component was removed very rapidly, leaving a synthetic polymer residue which was very slow to degrade [5]. As expected, both the PHBV and PHB films showed extensive weight loss. The remaining examples illustrate the effect of DS on composting rates of CA. For the CAs having a DS of 2.97 and 2.52, minimal weight loss was observed and the films remained intact. The film prepared from the CA with a DS of 2.21 underwent extensive breakage and discoloring and had a % weight loss of 38% after 14 days. Upon lowering the DS to 2.06, the films completely disintegrated and no pieces could be recovered from the compost.

· The time frame for complete disintegration and mineralization of a polymer during a composting operation is still subject to considerable debate. The likely outcome is that composting rates will be related to natural materials, e.g., oak leaves, under very controlled conditions. However, the data presented above illustrate that PCL, PHB, and CA (DS < 2.2) are excellent candidates as compostable polymers. The extent of their use for these applications will likely depend upon their physical properties and cost.

Cellulose Acetate/Triethylcitrate

Although cellulose acetate having a DS less than ca. 2.2 shows good composting rates, the question remains regarding the ability of the material to be thermally processed. As Kamide has shown and as our data indicate [21], when the T_m of cellulose acetate is plotted versus the DS, a minimum is observed near a DS of 2.3 (Fig. 2). Extrapolating horizontally across the minimum from a DS of 2.5 (common
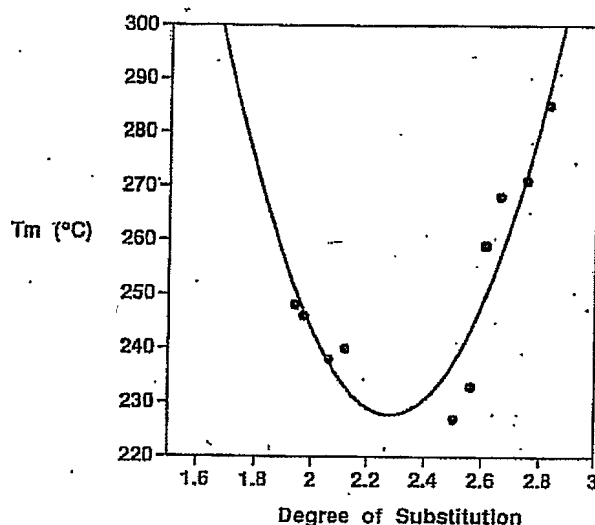
FIG. 2. A plot illustrating the change in nonequilibrium melting temperature as a function of cellulose acetate degree of substitution.

thermoplastic CA) to a lower DS suggests that a CA with a DS of 2.0 would be thermally processible. Indeed, we have found that thermal processing of CAs in the range of 2.0 to 2.2 to be very comparable to that of CA with a DS of 2.5.

To evaluate the compostability of CA/TEC mixtures, we prepared compression-molded films (28 and 30% TEC) as well as injection-molded bars (30–31% TEC) from CA with a DS of 2.05. In the case of the bars, three cellulose acetates with identical DS but differing in molecular weight were used. These materials were then subjected to our bench-scale composting. Figure 3 shows a typical compost temperature and % H_2O profile for a 30-day composting experiment. As can be seen, the peak thermophilic phase was reached in ca. 24 hours where it remained for ca. 2 days. The temperature then dropped over a period of 5 days to near 38°C. This maturation phase was then maintained for an additional 22 days. During the thermophilic phase, the % H_2O dropped to near 58% due to the secondary air flow used to cool the units. During the maturation phase with a lesser air flow, water was produced which slowly brought the water content back near 62–63% where it remained for the life of the experiment.

Figure 4 shows the % weight loss for the films and for the bars. In the case of Entry 5, the films extensively broke up and after 12 days the experiment was terminated as only very small, discolored chips could be found. For Entry 4, the film samples also extensively fragmented but samples were removed every 4–6 days for characterization. These removed samples, which were not subjected to the full composting cycle of 30 days, were included in the final weight loss which lowers the
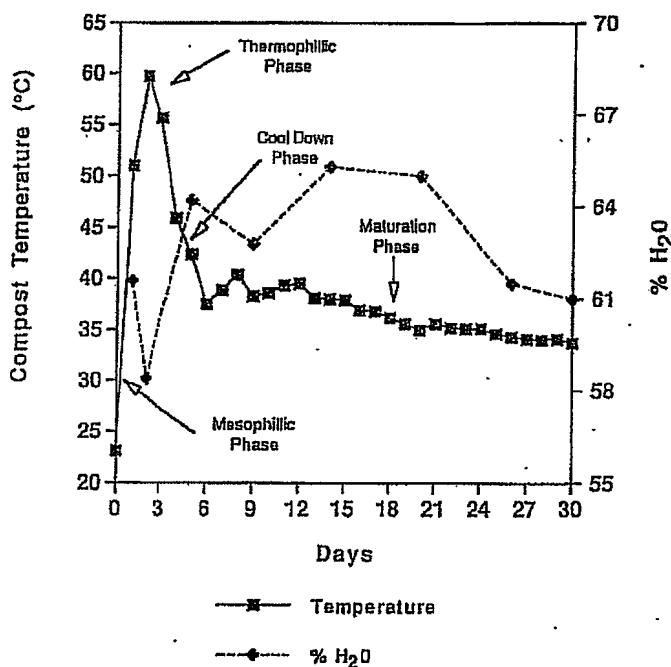

FIG. 3. A typical compost temperature profile and compost water content for composting experiments involving cellulose acetate/triethylcitrate.
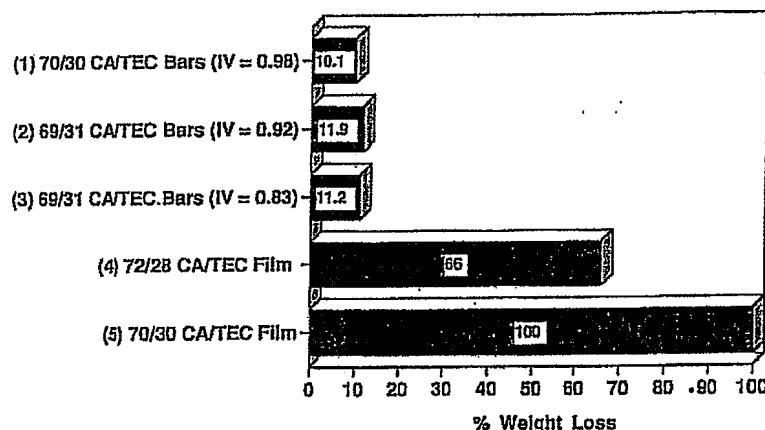
FIG. 4. The % weight loss observed for CA/TEC film and bars. The % weight loss for Entry 4 reflects the weight of samples removed at different time intervals during the composting experiment, and thus this apparent weight loss is the lower level of % weight loss.

apparent final weight loss. In the case of the injection-molded bars, the % weight loss was very similar but, as Fig. 5 illustrates, % weight loss does not adequately describe the results. Bars, which were not subjected to composting, were washed using our normal washing procedure [5]. In this case we found that 1.2, 0.3, and 0.0% TEC was removed from the bars having an IV of 0.98, 0.92, and 0.83, respectively. This behavior is likely related to the molecular weight dependence of diluent compatibility with a polymer. That is, TEC will diffuse more rapidly from the higher molecular weight CA. If one subtracts the TEC lost from the total % weight loss and assumes that the remaining weight loss is due to biodegradation of the CA, one can attempt to calculate the weight loss normalized to the total surface area [9]. In doing this, one finds that the bar prepared from the highest molecular weight CA has nearly twice the weight los (48.7 $\mu g/mm^2$) of that observed for the bar prepared from the lowest molecular weight CA (26.4 $\mu g/mm^2$). In the case of the middle molecular weight CA, the amount of TEC lost is greater than the total weight loss, indicating that diffusion of TEC from the bars is modified after composting! Clearly, unless the diluent is completely or nearly completely removed from the molded object, normalized weight loss cannot be used for polymer–diluent mixtures. In cases involving polymer–polymer blends where diffusion is not observed, this issue presents no difficulties.

As noted, film samples were removed for further characterization. Figure 6 shows the average DS and % TEC determined by ^{1}H NMR. As can be seen, the % TEC drops rapidly to below 1.5% while the measured DS declines more slowly over 14 days to near 1.7, dropping to 1.41 at 30 days. As we and others have noted [4, 9], degradation of cellulose acetate occurs at the surface of the substrate so that bulk values such as DS reflect the composition of the unchanged interior and the constantly changing surface. A profile such as that seen in Fig. 6 is typical of what we have observed many times for CA. Finally, Fig. 7 shows the molecular weight profile for these same samples as determined by GPC. In this case, M_w is observed
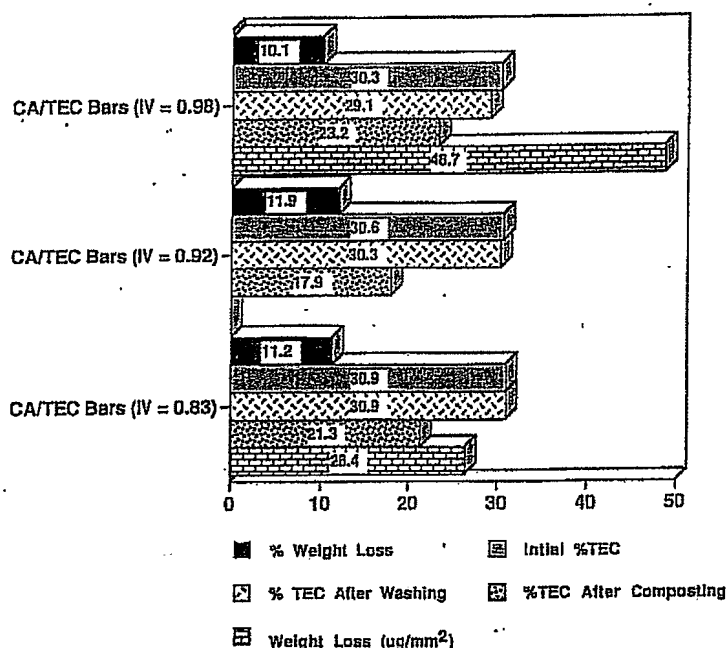
FIG. 5. The % weight loss, initial and final TEC content, and normalized weight loss for CA/TEC bars.

to decrease while M_n correspondingly increases. This would suggest preferential internal chain cleavage as opposed to cleavage from the chain end.

Cellulose Acetate Propionate/Aliphatic Polyester Blends

In a series of recent reports we have shown that CAP forms miscible blends with a variety of aliphatic polyesters such as poly(ethylene glutarate) (PEG) or poly(tetramethylene glutarate) (PTG) [16, 18, 19]. In general, these blends are stable, optically clear, amorphous polymer blends. As we have noted above, cellulose acetate propionates with a suitable low DS are expected to be biodegradable at a reasonable rate while highly substituted CAPs are expected to biodegrade very slowly. Linear, straight-chain, aliphatic polyesters, similar to those described in this account, have been demonstrated to be biodegradable [22]. Given this background, the interesting questions which naturally arise are by what mechanism do homogeneous mixed blends of these two polymers degrade and does the biodegradation of one polymer component influence the biodegradation of the other.

In this brief account we focus on the weight loss, molecular weight, and blend composition as a function of CAP DS, polyester type (PEG vs PTG), and polyester content of the blend. The percent weight loss for these blends are shown in Fig. 8 along with entries for CAP/PHB and CAP/PDDLA blends. The observed general trend is an increasing percent weight loss as the amount of polyester in the blend increases and as the DS of the CAP decreases. Little difference in weight loss is observed between the CAP/PEG and CAP/PTG blends at the same DS and polyes-
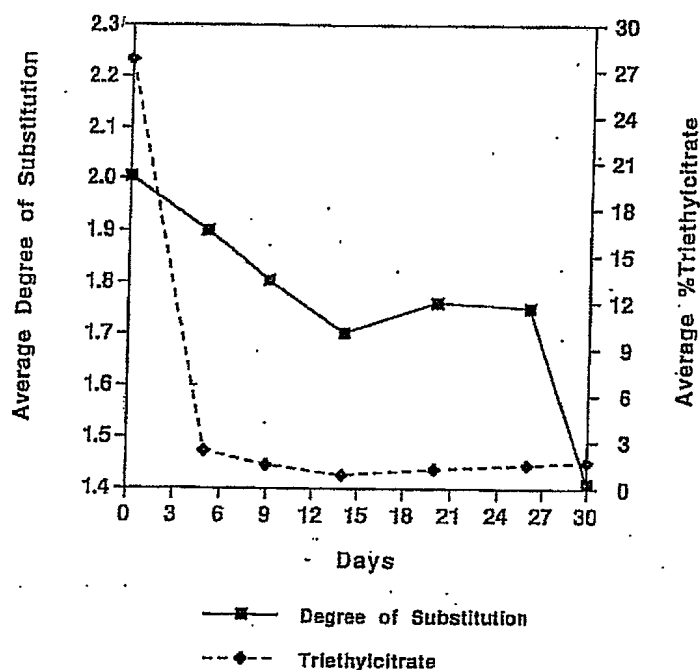
FIG. 6. · The change in DS and % TEC content of CA/TEC films removed and analyzed by ^{1}H NMR during a 30-day composting experiment.

ter content. For example, Entries 7 and 8, which differ only in polyester type and which were tested in the same composting experiment, show virtually no difference in weight loss. When the CAP DS is decreased to 2.15 and the weight percent of polyester is increased by 5%, the weight loss increases by 5–10%. Maximum weight loss was observed when the DS of the CAP was lowered slightly and when the PEG became the major component in the blend. Some variation is observed between composting experiments.

Of particular interest are the differences in weight loss between the CAP/PHB blend (Entry 4), the CAP/PDLLA blend (Entry 5), and the equivalent CAP/PEG, PTG blends (Entries 6–9). Although the CAP/PHB blend has a higher content of PHB relative to the CAP/PEG, PTG blends, only 5% weight loss is observed after a 30-day composting cycle for the CAP/PHB blend versus a 20–25% weight loss observed for the CAP/PEG, PTG blends (cf. Entries 5–8) in a 10–15-day composting cycle. For the CAP/PDLLA blend, a 10% weight loss is observed which is half of the equivalent CAP/PTG blend (Entry 8) where a 20% weight loss was observed. In the past, we and others have proposed that the initial step in the biodegradation of cellulose esters involves attachment of enzyme(s) to the substrate. Biologically (esterase) mediated hydrolysis of the acetyl substitutent provides chains or chain segments with no or little substitution which can then be degraded by cellulases by a process that has been extensively studied [23]. By this mechanism, biodegradation occurs on the surface of the substrate with the effect of surface erosion. With the exception of PHB, which degrades by a mechanism similar to cellulose [24], it is
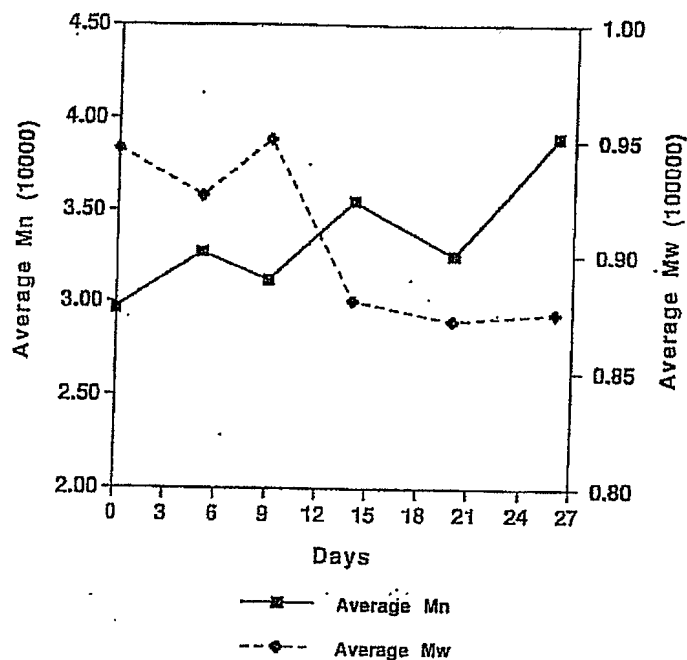
FIG. 7. The change in number-average and weight-average molecular weight for CA/TEC films removed and analyzed by GPC during a 30-day composting experiment.
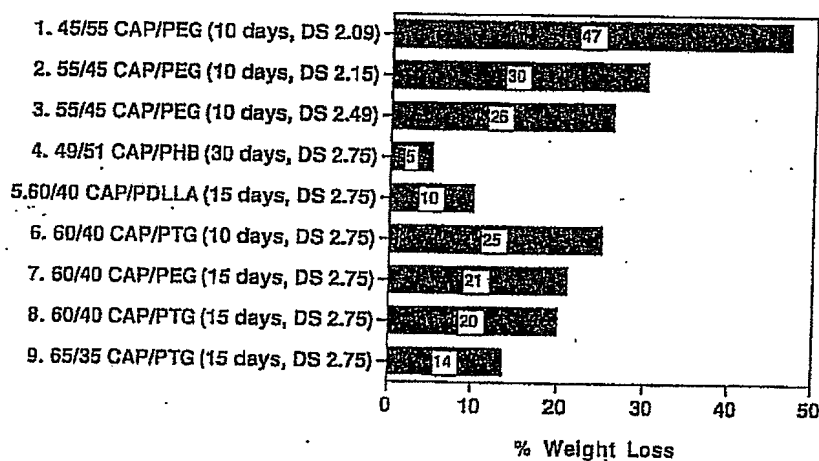

FIG. 8. Weight loss for blends of cellulose acetate propionate and aliphatic polyesters after composting. The initial ratio provides the blend compositions. The length of the composting cycle in days and the DS·of the CAP are provided within the parentheses.
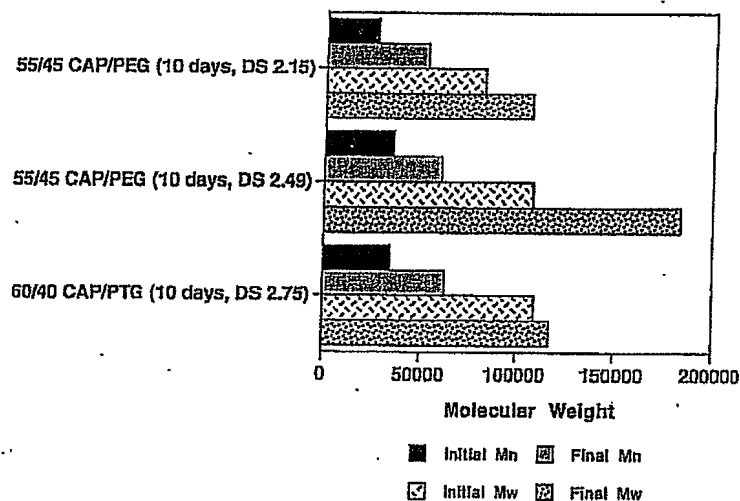
FIG. 9.   The change in weight-average and number-average molecular weights for selected CAP/aliphatic polyester blends after composting.
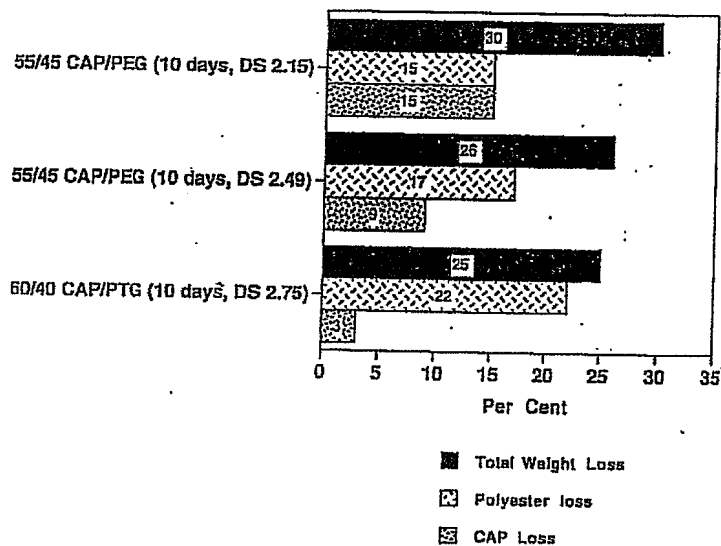

FIG. 10.   The total % weight loss, polyester loss, and CAP loss for CAP/aliphatic polyester blends after composting.

generally believed that polyesters are first hydrolytically degraded to monomers or short-chain oligomers which are then assimilated by microorganisms [22]. Most likely, for aliphatic polyesters, both chemical and biological hydrolysis occur concurrently. In the case of chemical hydrolysis, prior attachment of enzyme to substrate is not required and hydrolytic (nonbiological) degradation can occur both on the surface and in the interior of the substrate. Given this background, this would suggest that the weight loss in the PEG or PTG blends containing highly substituted CAP is probably due to initial hydrolysis of the PEG or PTG.

Figure 9 provides the initial and final molecular weights for three blends from a 10-day compost experiment. In all cases both the number-average and weight-average molecular weights increased. This would be consistent with preferential loss of the lower molecular weight polyester. A better understanding of what is occurring with these blends can be obtained from Fig. 10 where the total % weight loss is plotted versus the weight loss of polyester from the blend (determined by ^{1}H NMR). If only polyester was degrading while the CAP remained intact, then the % weight loss and the polyester loss should be equal. For the blend involving the DS = 2.75 CAP, the polyester loss and the total weight loss are nearly equal. However, at a DS of 2.15 only half of the weight loss can be ascribed to the polyester. This would indicate that for the highly substituted CAP, the polyester is degrading rapidly with little loss of CAP, while both blend components are degrading at lower degrees of substitution.

CONCLUSION

In this work we have evaluated in our bench-scale composting system many polymers which have been proposed for use as compostable polymers. Cellulose acetate (DS < 2.2), PHBV, and PCL exhibited the fastest composting rates, completely disappearing after 14 days. Each of these materials has different strengths and weakness. PLA has many desirable physical properties and has good potential if it can be made successfully on an industrial scale. We were somewhat surprised at the composting rate of our PLA relative to PHB or PCL. Matter-Bi is presently commercially available and has found use in different applications. The issue of mineralization of the nonstarch components of Matter-Bi needs to be resolved. Polyalkanoates, e.g., PHB, are generally produced commercially by fermentation. The most notable properties of PHB are its good barrier properties and excellent composting rates while the major shortcomings of PHB are its low T_g and slow crystallization rates. Both PCL and CA are produced on a larger scale than PHB and, at least for the near term, can be obtained at a lower cost. Polycaprolactone has many excellent properties. The primary problem with PCL is its low T_m which somewhat limits its use. Cellulose acetate, perhaps one of the oldest thermoplastics known, has been used in a very broad range of applications and its properties are well understood. The major difficulty with cellulose esters is that they generally must be plasticized in order to be thermally processed without decomposition or loss of physical properties.

In view of the need for placticization of cellulose esters in thermoplastic applications, we have presented preliminary studies involving CA/TEC and CAP/aliphatic polyesters. CA/TEC films disappeared rapidly upon composting while the

injection-molded bars exhibited weight losses of 10–12%. For the CAP/aliphatic polyester blends, the type of polyester (PEG versus PTG) in the blend made no difference in composting rates. In general, as the DS of the CAP decreased and the amount of polyester in the blend increased, the rate of composting and the weight loss due to composting increased. When the CAP was highly substituted, almost all of the weight loss was ascribed to loss of polyester. When the DS of the CAP was below approximately 2.0, both components were observed to degrade. The observed weight loss due to composting for CAP/polyalkanoates (PDLLA and PHB) blends was less relative to the CAP/PEG, PTG blends. This work also points out some of the difficulties surrounding the study of the biodegradation of compositions containing two or more components.

REFERENCES

[1] (a) R. A. Clendinning, J. E. Potts, and W. D. Niegisch, US Patent 3,844,987 (1974). (b) R. A. Clendinning, J. E. Potts, and W. D. Niegisch, US Patent 3,850,862 (1974). (c) R. A. Clendinning, J. E. Potts, and W. D. Niegisch, US Patent 3,850,863 (1974). (d) R. A. Clendinning, J. E. Potts, and W. D. Niegisch, US Patent 3,932,319 (1976). (e) J. E. Potts, R. A. Clendinning, W. B. Ackart, and W. D. Niegisch, *Polym. Sci. Technol.*, *3*, 61 (1973).

[2] (a) G. Lay, B. Bellingen, J. Rehm, R. F. Stepo, M. Thoma, J.-P. Sachetto, D. J. Lentz, and J. Silbiger, US Patent 5,095,054 (1992). (b) C. Bastioli, V. Bellotti, G. Del Tredici, R. Lombi, A. Montino, and R. Ponti, International Publication WO 92/19680 (1992).

[3] (a) M. Yasin and B. J. Tighe, *Plas., Rubber, Compos. Process. Appl.*, *19*, 15 (1993). (b) H. Nishida and Y. Tokiwa, *J. Environ. Polym. Degrad.*, *1*, 65 (1993). (c) Y. Kumagai and Y. Doi, *Makromol. Chem., Rapid Commun.*, *13*, 179 (1992). (d) Y. Kumagai and Y. Doi, *Polym. Degrad. Stab.*, *35*, 87 (1992). (e) Y. Kumagai and Y. Doi, *Ibid.*, *36*, 241 (1992). (f) Y. Kumagai and Y. Doi, *Ibid.*, *37*, 253 (1992). (g) J. E. Kemnitzer, S. P. McCarthy, and R. A. Gross, *Macromolecules*, *25*, 5927 (1992).

[4] C. M. Buchanan, R. M. Gardner, and R. J. Komarek, *J. Appl. Polym. Sci.*, *47*, 1709 (1993).

[5] R. M. Gardner, C. M. Buchanan, R. J. Komarek, D. D. Dorschel, C. Boggs, and A. W. White, *Ibid.*, *52*, 1477 (1994).

[6] R. J. Komarek, R. M. Gardner, C. M. Buchanan, and S. C. Gedon, *Ibid.*, *50*, 1739 (1993).

[7] C. J. Rivard, W. S. Adney, M. E. Himmel, D. J. Mitchell, T. B. Vinzant, K. Grohmann, L. Moens, and H. Chum, *Appl. Biochem. Biotech.*, *34/35*, 725 (1992).

[8] J.-D. Gu, M. Gada, G. Kharas, D. Eberiel, S. P. McCarthy, and R. A. Gross, *J. Am. Chem. Soc., Polym. Prepr.*, p. 351 (1992).

[9] J.-D. Gu, D. Eberiel, S. P. McCarthy, and R. A. Gross, *J. Environ. Polym. Degrad.*, *1*, 143 (1993).

[10] R. A. Gross, J.-D. Gu, D. Eberiel, M. Nelson, and S. P. McCarthy, in *Fundamentals of Biodegradable Materials and Packaging* (D. Kaplan, E.

Thomas, and C. Ching, Eds.), Technomic Publishing Co., Lancaster, Pennsylvania, 1993.

[11]   C. M. Buchanan, R. M. Gardner, R. J. Komarek, S. C. Gedon, and A. W. White, *Ibid.*, p. 133.

[12]   (a)   U. Kasulke, H. Dautzenberg, E. Polter, and B. Philipp, *Cellul. Chem. Technol.*, *17*, 423 (1983). (b)   A. S. Perlin and S. S. Bhattacharjee, *J. Polym. Sci., Part C, 36*, 506 (1971). (c) M. G. Wirick, *J. Polym. Sci., Part A-1, 6*, 1965 (1968).

[13]   F. Stutzenberger and G. Kahler, *J. Appl. Bacteriol., 61*, 225 (1986).

[14]   E. T. Reese, *Ind. Eng. Chem., 49*, 89 (1975).

[15]   P. A. Cantor and B. J. Mechalas, *J. Polym. Sci., Part C, 28*, 225 (1969).

[16]   C. M. Buchanan, S. C. Gedon, A. W. White, and M. D. Wood, *Macromolecules, 26*, 2963 (1993).

[17]   C. M. Buchanan, K. J. Edgar, J. A. Hyatt, and A. K. Wilson, *Ibid., 24*, 3050 (1991).

[18]   C. M. Buchanan, S. C. Gedon, B. G. Pearcy, A. W. White, and M. D. Wood, *Ibid., 26*, 5704 (1993).

[19]   C. M. Buchanan, S. C. Gedon, A. W. White, and M. D. Wood, *Ibid., 25*, 7373 (1992).

[20]   A. W. White, C. M. Buchanan, B. G. Pearcy, and M. D. Wood, *J. Appl. Polym. Sci., 52*, 525 (1994).

[21]   K. Kamide and M. Saito, *Polym. J., 17*, 919 (1985).

[22]   A.-C. Albertsson and O. Ljungquist, *J. Macromol. Sci.—Chem., A23*(3), 393 (1986).

[23]   M. Shimada and M. Takahashi, in *Wood and Cellulosic Chemistry* (D. N.-S. Hon and N. Shiraishi, Eds.), Dekker, New York, 1991, p. 621.

[24]   Professor Yoshiharu Doi, The Institute of Physical and Chemical Research, Japan, Paper Presented at the 2nd Bio/Environmentally Degradable Polymer Society Meeting, Chicago, Illinois, 1993.